Low-Cost Planar Na-Metal Halide Batteries

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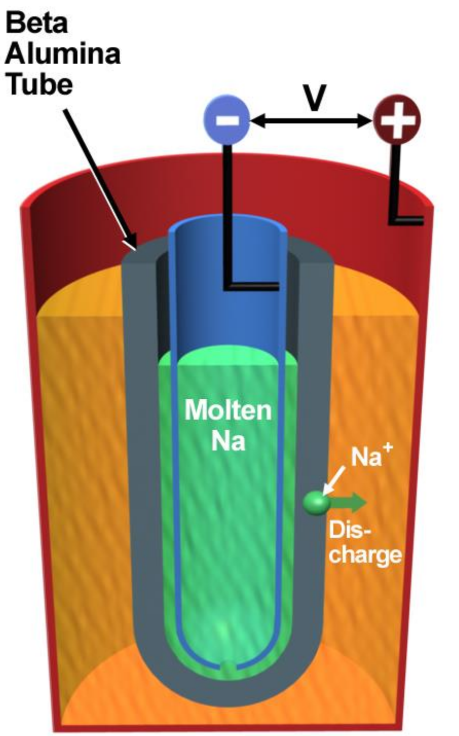
Sponsored by DOE Office of Electricity Energy Storage Program – Program Manager: Dr. Imre Gyuk

Sodium β"-Alumina Batteries (NBBs)

- **Batteries consisting of *molten sodium anode* and *β"-Al_2O_3 solid electrolyte* (BASE).**
  - Use of low-cost, abundant sodium → low cost
  - High specific energy density (120~240 Wh/kg)
  - Good specific power (150-230 W/kg)
  - Good candidate as a large-scale energy storage Device for renewable energy
  - Operated at relatively high temperature (300~350°C)



- **Sodium-sulfur (Na-S) = battery**
  - **$2Na + xS \rightarrow Na_2S_x$** (x = 3~5)
    - E = 2.08~1.78 V at 350°C
- **Sodium-nickel chloride (Zebra) battery**
  - **$2Na + NiCl_2 \rightarrow 2NaCl + Ni$**
    - E = 2.58V at 300°C
    - Use of catholyte ($NaAlCl_4$)
  - **Merits**
    - Safe cell failure mode
    - Easiness of assembly in discharged state
    - Less corrosive nature of cathode materials

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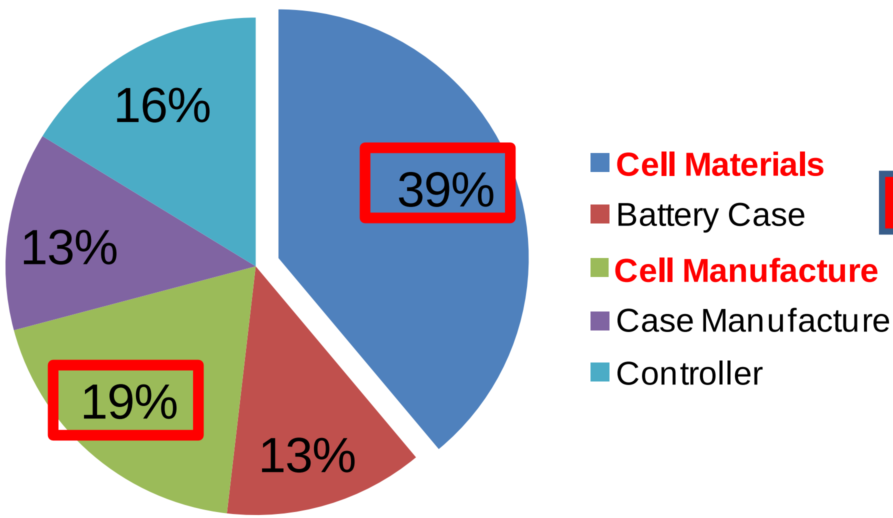
ZEBRA battery cost projection*

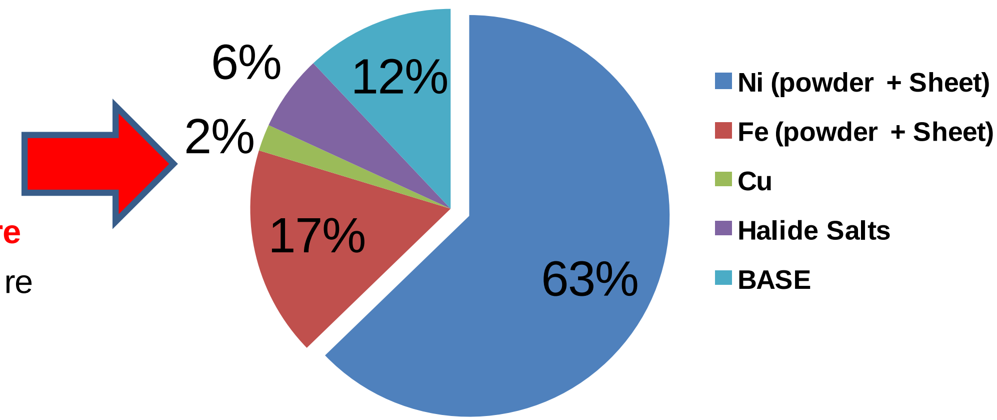
ZEBRA battery cost

$1540/Battery (21.2kWh)



Cell material cost

$/kWh



* R.C. Galloway, C.-H. Dustmann, “ZEBRA Battery - Material Cost, Availability and Recycling”, MES-DEA GmbH, EVS 20, 2003.

- **Obstacle for commercialization**
  - Relatively expensive ➔ **Cost reduction** is a key issue to commercialize this technology for large energy storage applications.

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Approaches to Reduce Cost

- **Intermediate Temperature (≤200°C) Na-$NiCl_2$ Battery**
  - Use of economical construction materials and manufacturing processes such as polymer seals, enabling high throughput manufacturing methods
    - Not using high-cost processes such as glass sealing or TCB
    - Low capital cost and manufacturing cost
  - Low maintenance cost
  - Better cycle life by suppressing degradation mechanisms

- **Battery with Low-Cost Active Materials**
  - Replacement of nickel with low-cost zinc or iron

Previous Results

- Improved stability of Na-$NiCl_2$ Battery at reduced temperature less than 200°C
- Development of low-melting point catholyte based NaCl-NaBr-$AlCl_3$
- Overcoming the wetting problem of Na melt at intermediate temperature using metalized layer
- Development of Zn-based battery with $NaAlCl_4$ catholyte

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2014 Goals and Accomplishments

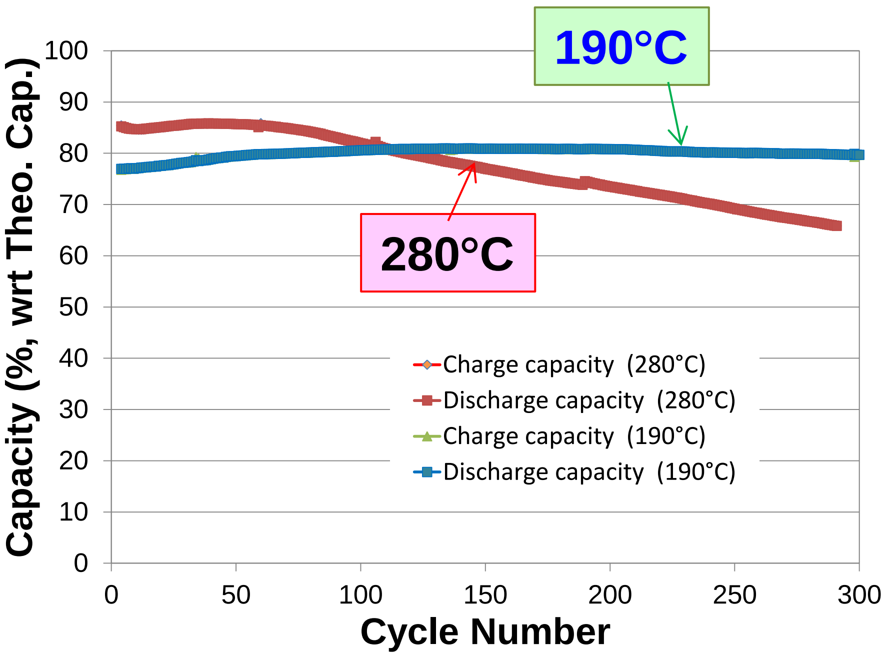
- **Intermediate Temperature Operation of $Na\text{-}NiCl_2$ Cell**
  - **Long-Term Test** : Ran at 190°C over 1800 cycles with <1%/1000 cycles degradation and 90% energy Efficiency
  - Developed **polymer seals**
- **Multi-cell Module**
  - 2-cell module (32 cm^2 active per cell)
  - Compressive polymer seals with a load frame
  - Achieved properties/(Target) @ 50 mW/cm^2 Discharge:
    - Energy Efficiency: **94%** /(>90%)
    - Degradation: **0.46%/100** cycles /(<1%/100 cycles)
- **Fe-Based Battery:**
  - >40% reduction in materials cost expected compared to Ni.
  - Developed low-temperature cell activation technology using sodium polysulfide
- **BASE Fabrication at lower temperature (1400°C)**
  - Simultaneous sintering and conversion
  - Densification of β” alumina assisted by transition-metal doped YSZ

Performance of IT Na-$NiCl_2$ Cell

▶ 190°C vs. 280°C (cycled between 2.0~2.8V)

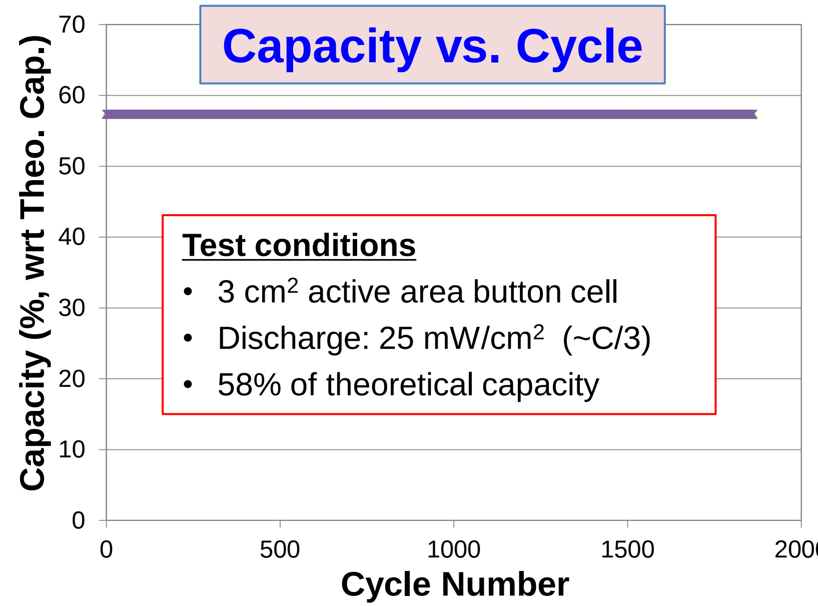
Test conditions

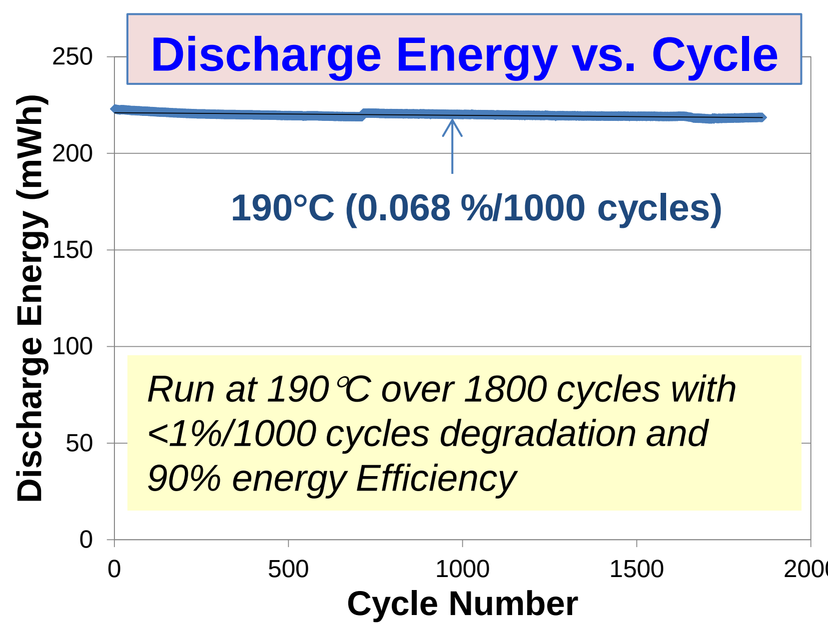
- 3 cm^2 active area button cell
- Current: 10 mA/cm^2 (~C/3)
- Cycled over 80% of theoretical capacity to enhance degradation



More stable cycling behavior was observed @ 190℃.

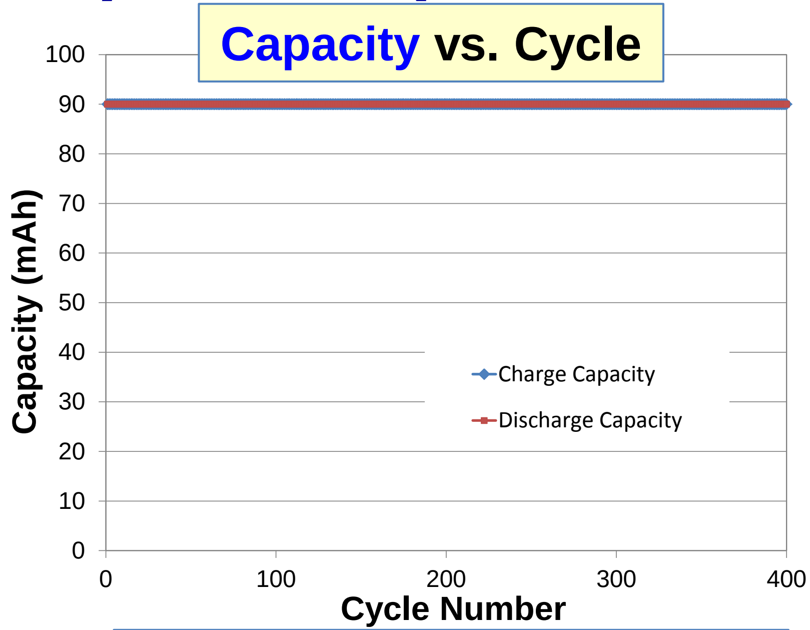
▶ Long-Term Performance at 190°C

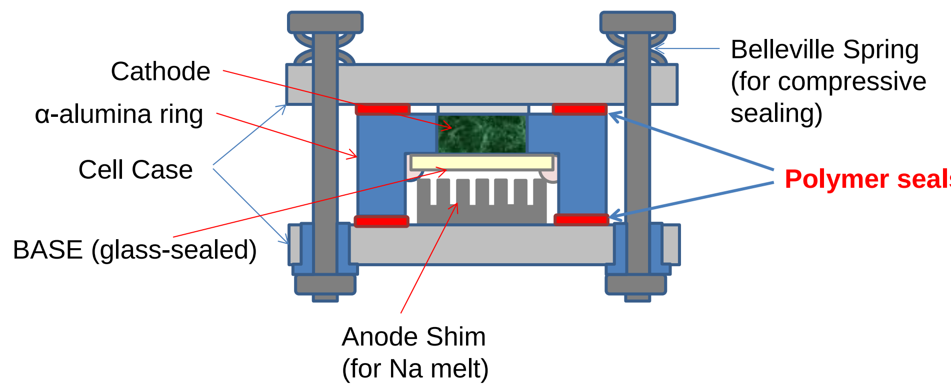


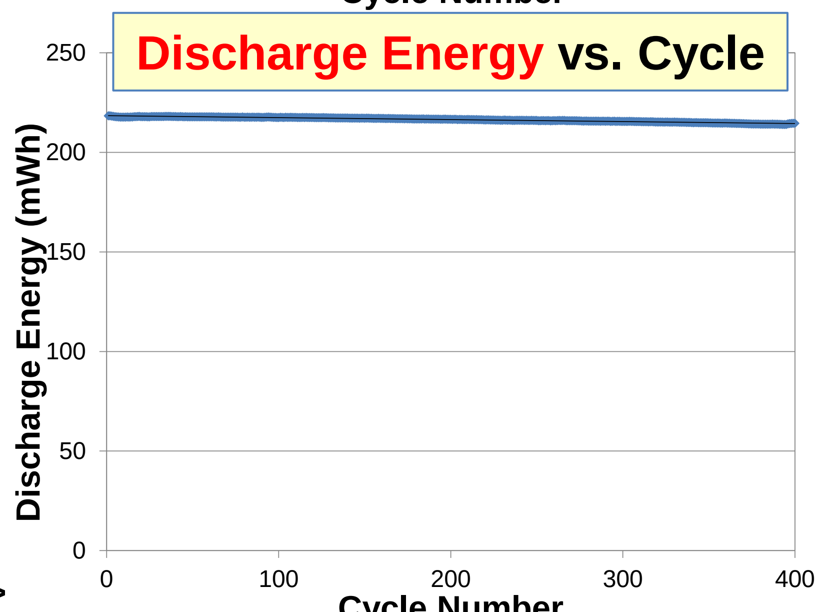


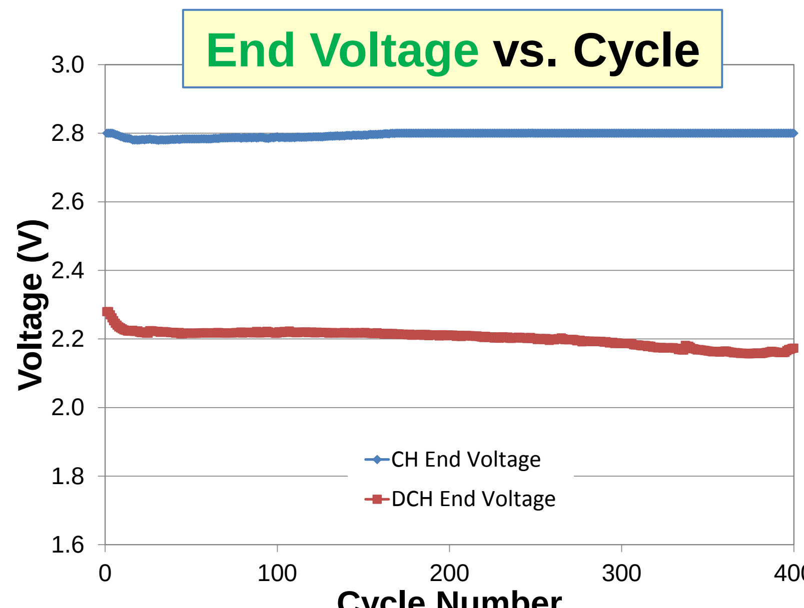
Polymer Seals (3 cm^2 Active Area)

- **Polymer Seals (Cathode/Anode): 25 mW/cm^2 (~C/3) DCH @ 190°C**



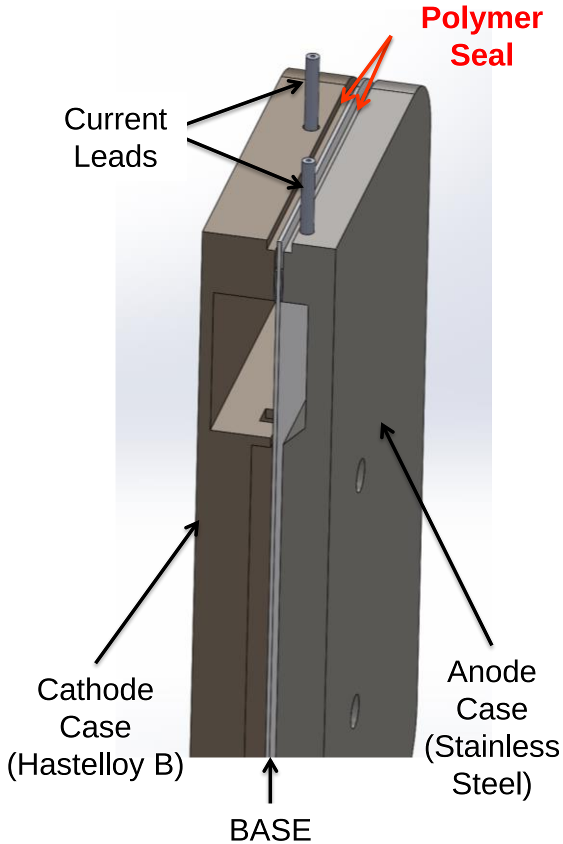


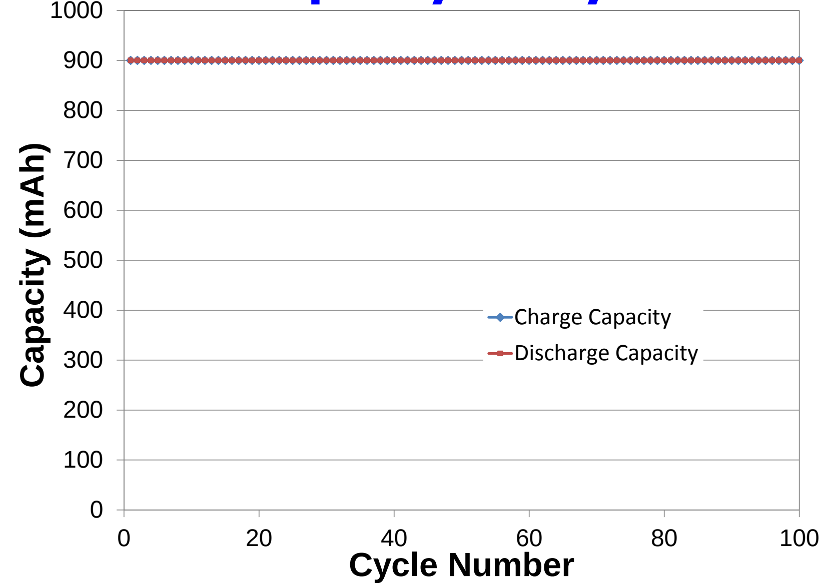


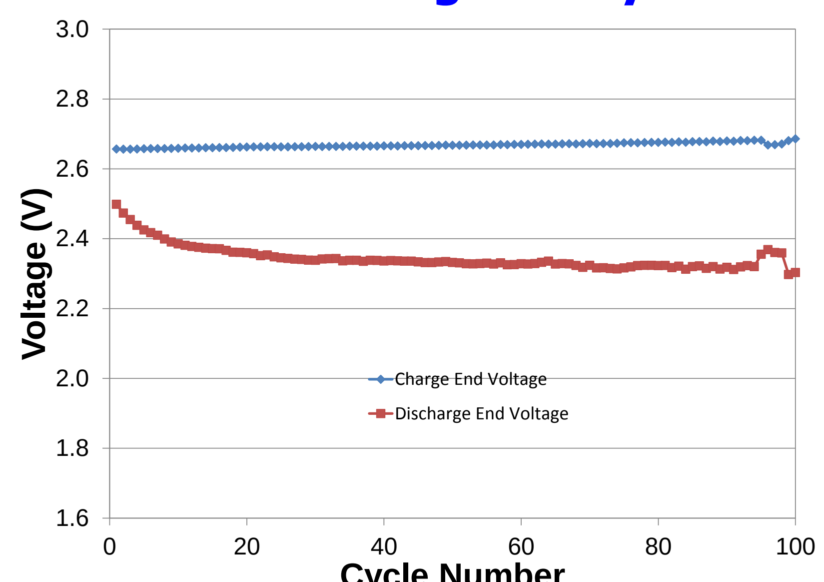


Large Cell (32 cm^2 Active Area) w/ Polymer Seal

▶ Unit Cell



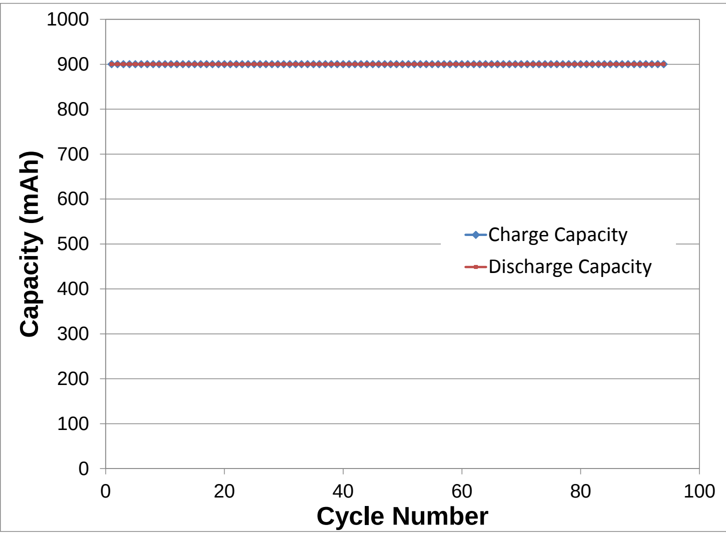




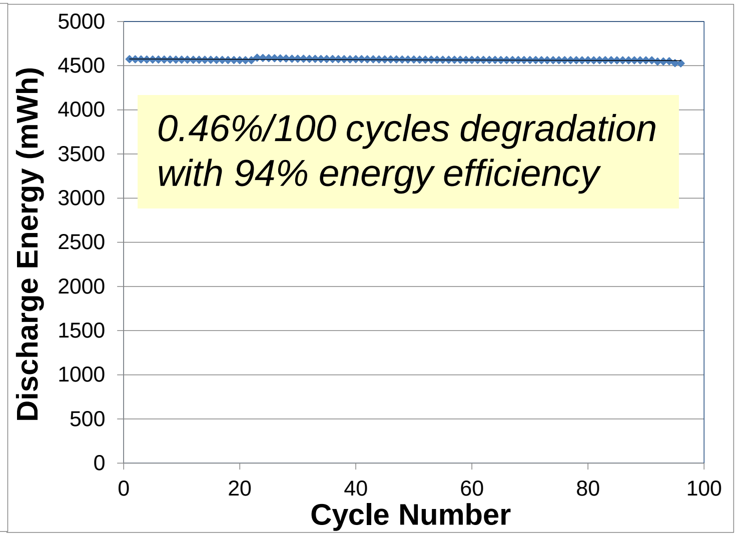
- Polymer seal with a load frame for both cathode and anode seals
- Cycled in a glove box, cooled down and moved outside
- C/4.5 Charge and 25 mW/cm^2 Discharge (~C/3) in air

2-Cell Module (32 cm² Active Area) w/ Polymer Seal

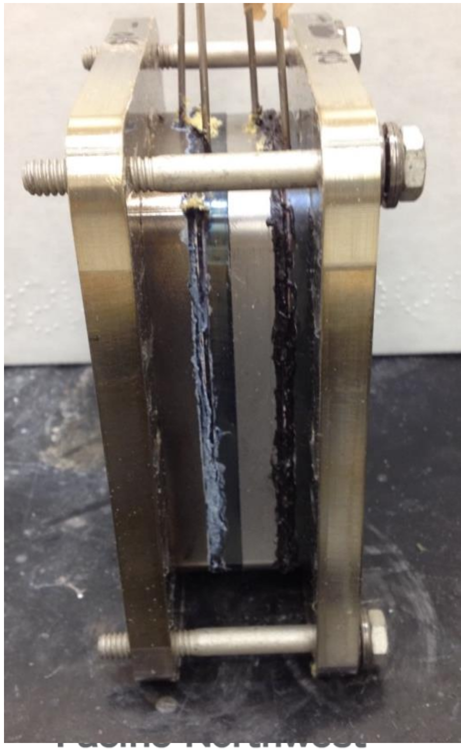
Capacity vs. Cycle



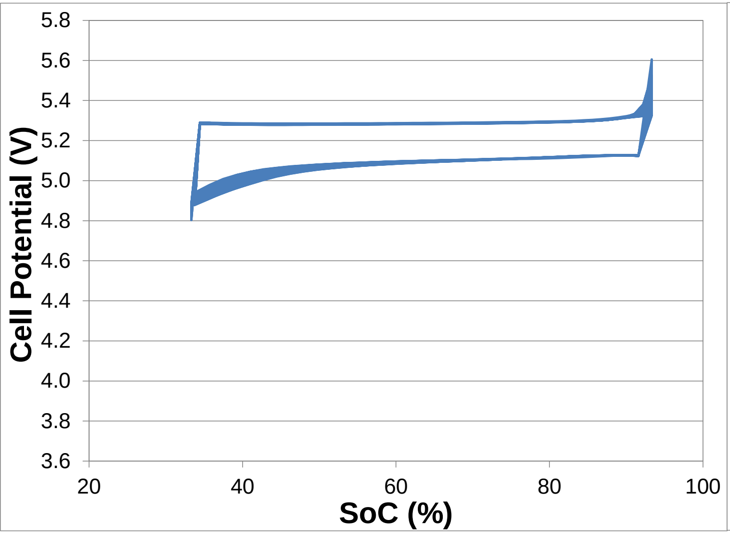
Discharge Energy vs. Cycle



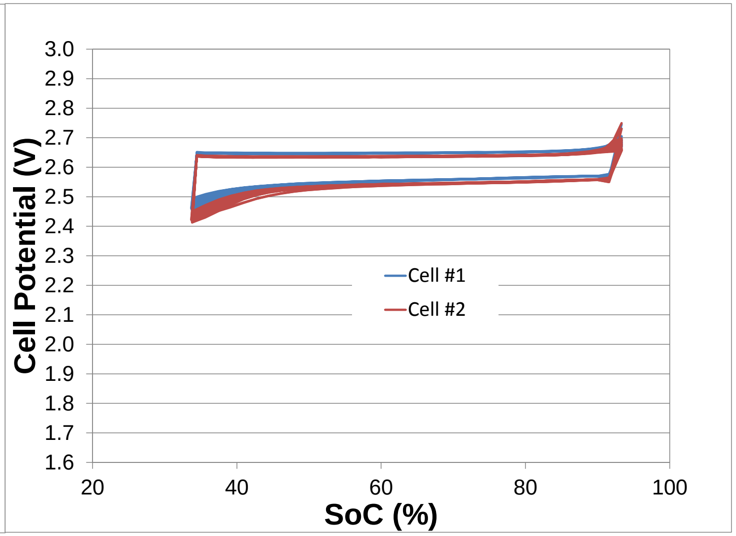
- 2 Cells connected in series with a load frame
- C/4.5 Charge and 50 mW/cm² Discharge (~C/3)



V vs. SOC (Module)



V vs. SoC (Each Cell)



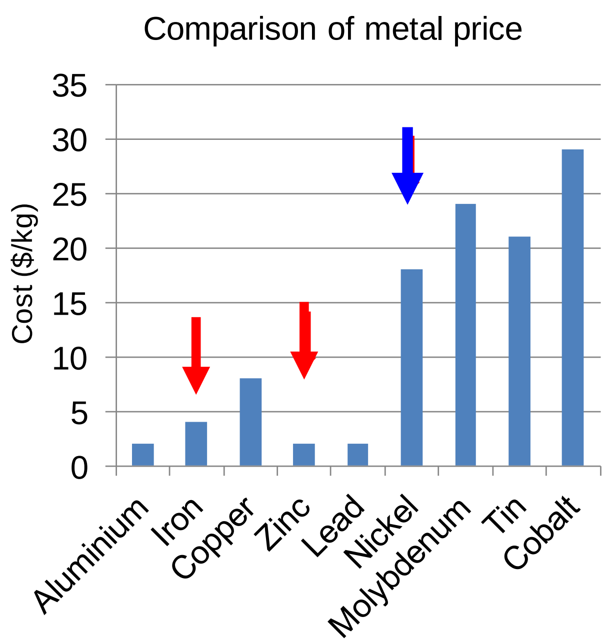
Na-Metal Halide Batteries: Ni vs. Zn or Fe

World production and reserves

	2005 World Production	World Reserves[a]
Aluminum	31,900,000	Large
Iron	1.38E+09	7.2E+10
Copper	15,000,000	430,000,000
Zinc	10,000,000	200,000,000
Lead	3,300,000	61,000,000
Nickel	1,400,000	56,000,000
Molybdenum	180,000	7,800,000
Tin	300,000	5,500,000

Unit: MT

[a] Based on the proven and probable portion of the world reserves.



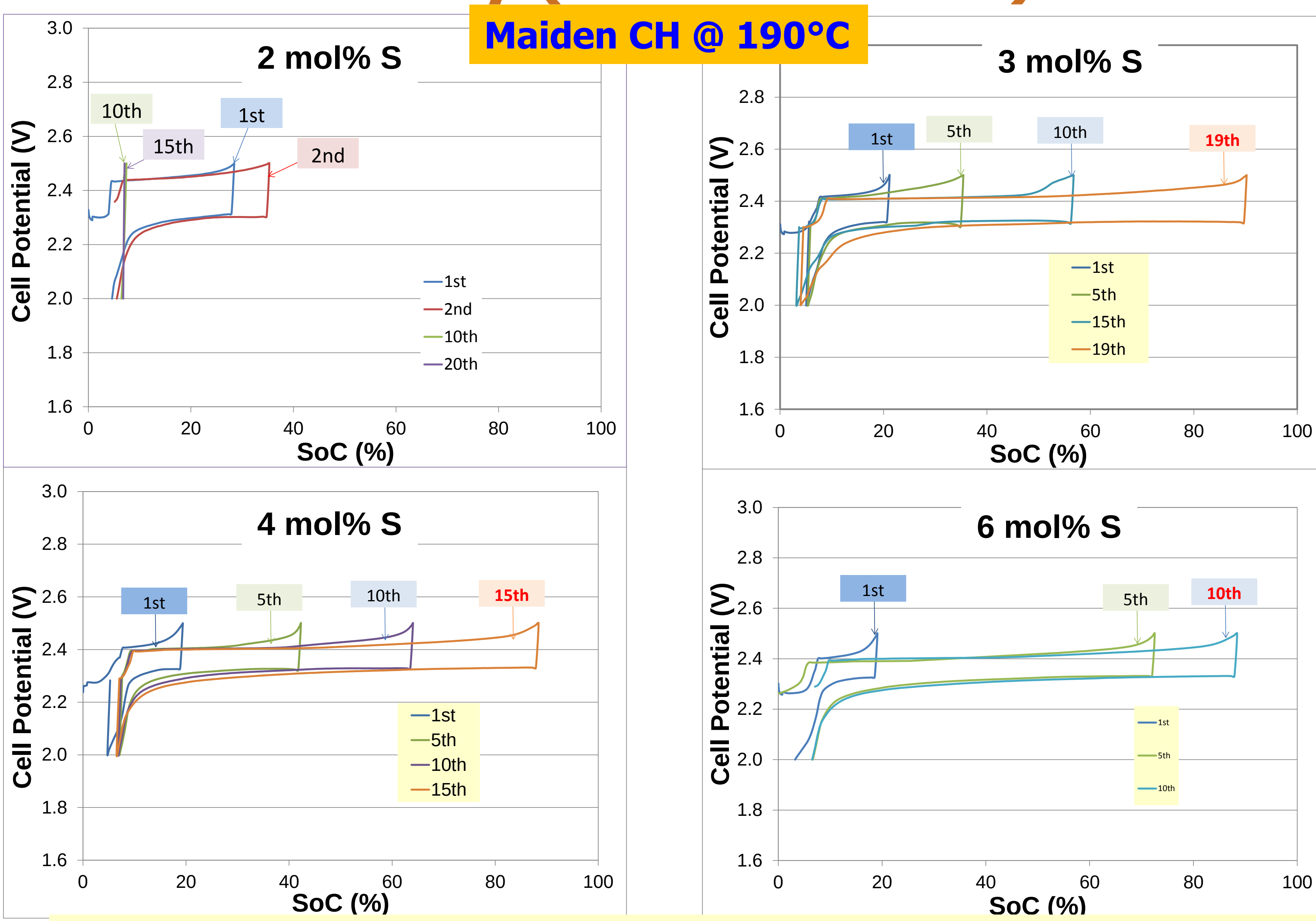
New Na-ZnCl$_2$ Battery

- Cathode consists of active materials (NaCl + Zn), $NaAlCl_4$ catholyte, and electrically conducting materials (metals, carbon, etc) in the form of powder, foam, mesh, etc.
- Assembled in discharged state (no addition of sodium in anode)
- Stable performance above the eutectic temperature (253°C) due to the liquid phase formation
- However, the relatively high operating temperature limits the use of polymer seals.

IT Fe-Based Na Battery (≤200°C)

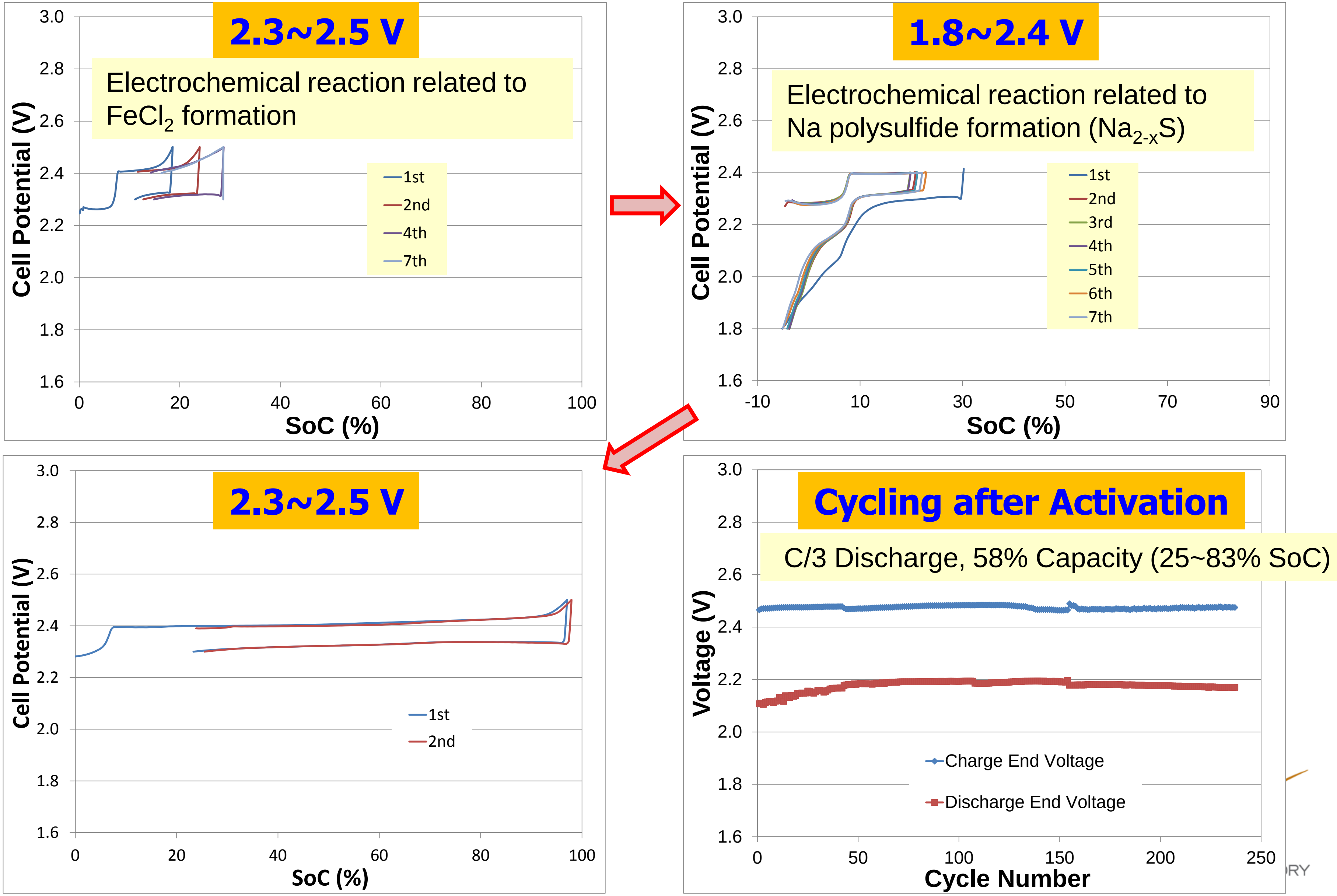
- **Technical Challenge**: Na-FeCl$_2$ battery is **not activated** due to the surface oxide layer on Fe particles when being assembled in a discharged state ➔ Additives to remove the passivation layer of Fe particles

Fe-Based Battery (Sulfur Content)



The amount of additives plays a critical role in initial activation and subsequent cell performance.

Fe-Based Battery (6 mol% sulfur)



The formation of Na polysulfide is in charge of Fe cell activation.

BASE Fabrication @ Lower Temperature

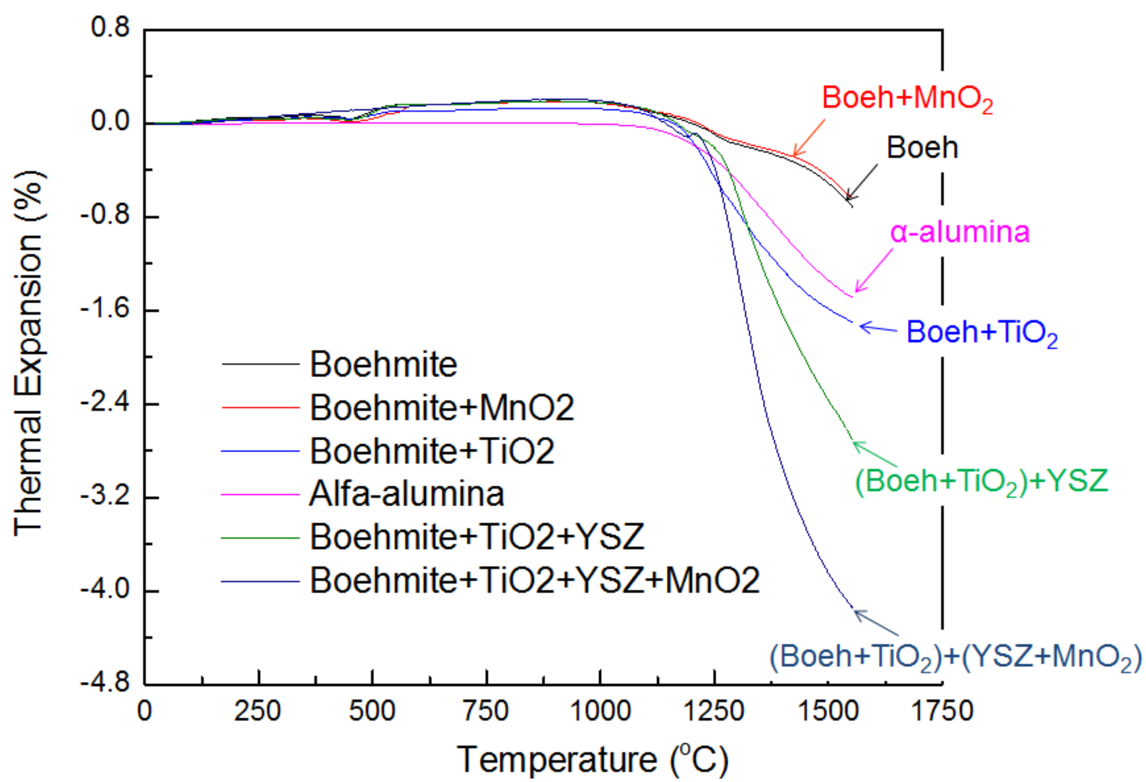
- **Difficulty to sinter β" alumina**
  - High temperature required (1600°C)
  - Loss of β" stabilizing elements (Na, Li, etc) at high temperatures

- **Conversion Process (Virkar, et al. US Patent#: 6,117,807)**
  - Two-step process
    - Sintering: α-alumina/YSZ (~1600°C)
    - Conversion of α-alumina to β"-alumina in β"-alumina beds (~1400°C)
  - YSZ: (i) Oxygen transport path during conversion, (ii) Strengthen the BASEs
  - Merits
    - Easy control of β" stabilizing elements
    - Strong composite structure
  - Drawbacks
    - Two-step process (Batch Process)
    - Waste β"-alumina powder used in conversion

Simultaneous Sintering/Conversion

▶ Transition-metal doped YSZ assisted densification of β" alumina

- Transition metal (TM) doped YSZ enhances the densification of β" alumina at relatively lower temperature (~1400°C), minimizing the loss of β" stabilizing elements (Na, Li, etc)
- Cosintering of Boehmite with Na, Li, and Ti salts and TM-doped YSZ



**1X Na nitrate and Li nitrate was added to all Boehmite samples*

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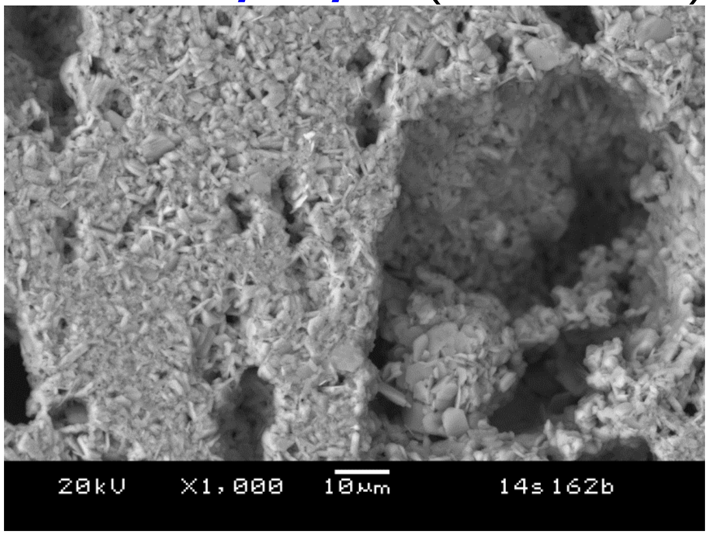
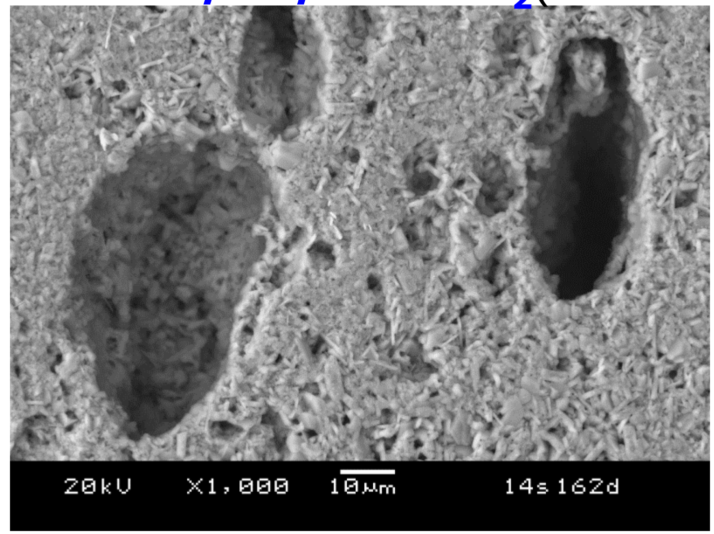
Densification @ 1400°C

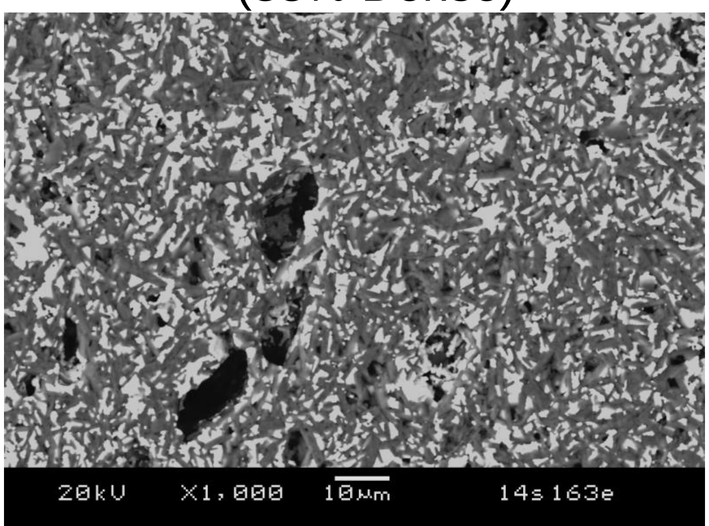
Boehmite/Na/Li (**38**% Dense)



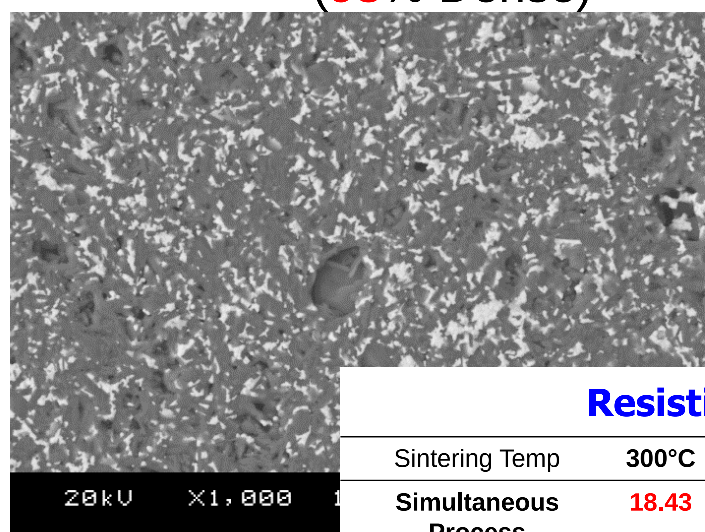
Boehmite/Na/Li +TiO_2(**60**% Dense)



(Boehmite/Na/Li +TiO_2) + **YSZ**
(**83**% Dense)



(Boehmite/Na/Li +TiO_2)+**(YSZ+MnO_2)**
(**98**% Dense)



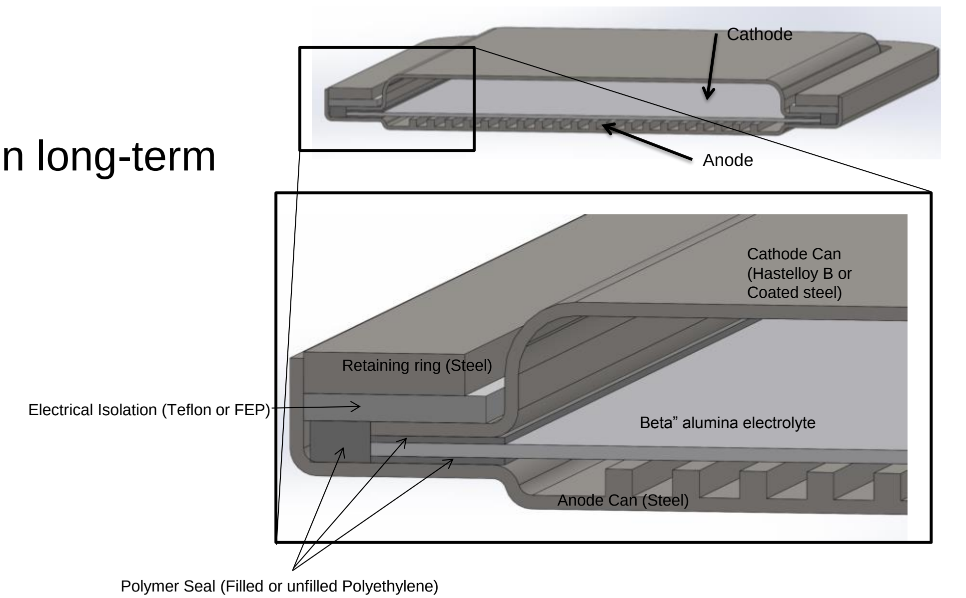
Resistivity

Sintering Temp	300°C	250°C	200°C	150°C
Simultaneous Process	**18.43**	23.40	**42.12**	78.54
Two-Step Sintering & Conversion	**26**	41	**72**	120

Future Work

IT multi-cell module

- New mass-producible design
- Long-term test and improvement in long-term stability
- Fe-based cell



Fe-based cell

- Study of activation mechanisms and performance optimization
- Long-term tests

Simultaneous sintering/conversion

- Cell tests

Acknowledgements

- **US DOE Office of Electricity – Dr. Imre Gyuk, Energy Storage Program Manager**

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Publications/Patents

- **15 invention reports**
- **5 US patent applications**
- **10 journal papers (including one in Nature Com.)**

1) X. Lu, G. Li, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z. Yang, "The Effects of Temperature on the Electrochemical Performance of Sodium-Nickel Chloride Batteries", J. Power Sources 215 (2012) 288
2) G. Li, X. Lu, C.A Coyle, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z. Yang, "Novel ternary molten salt electrolytes for intermediate-temperature sodium/nickel chloride batteries," J. Power Sources 220 (2012) 193
3) X. Lu, J.P. Lemmon, J.Y. Kim, V.L. Sprenkle, Z.G. Yang, "High Energy Density Na-S/NiCl2 Hybrid Battery," Journal of Power Sources 224 (2013) 312
4) D. Reed, G. Coffey, E. Mast, N. Canfield, J. Mansurov, X. Lu, Vince Sprenkle, "Wetting of sodium on β"-Al2O3/YSZ composites for low temperature planar sodium-metal halide batteries," Journal of Power Sources 227 (2013) 94
5) X. Lu, B.W. Kirby, W. Xu, G. Li, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z.G. Yang, "Advanced Intermediate-Temperature Na-S Battery," Energy & Environmental Science 6 (2013) 299
6) X. Lu, G. Li, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z. Yang, "A Novel Low-Cost Sodium-Zinc Chloride Battery," Energy & Environmental Science 6 (2013) 1837
7) G. Li, X. Lu, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, "Cell Degradation of Na-NiCl2 (Zebra) Battery," J. Mater. Chem. (2013) 14935
8) G. Li, X. Lu, J.Y. Kim*, J.P. Lemmon, and V.L. Sprenkle, "Improvement in cycling behavior of ZEBRA battery operated at intermediate temperature of 175□C ," Journal of Power Sources, 249 (2014) 414
9) G. Li, X. Lu, J.Y. Kim, D. Mei, J.P. Lemmon, V.L. Sprenkle, J. Liu, "Liquid Metal Electrode to Enable Ultra-Low Temperature Sodium-Beta Alumina Batteries for Renewable Energy Storage," Nature Communications (2014) vol. 5, 5, Article number: 4578.
10) G. Li, X. Lu, J.Y. Kim, M.H. Engelhard, J.P. Lemmon, and V.L. Sprenkle, "The Role of FeS on Initial Activation and Performance Degradation of Na-NiCl2 (ZEBRA) Battery," Journal of Power Sources, in press